Inorg. Chem. **2003**, *42*, 1901–1907

Inorganic Chemistry

Article

Spectroscopic and Thermal Investigations of the Fluoroaluminate Complex Formation in NaF–KF and LiF–NaF–KF Eutectics

J. H. von Barner,*,† C. Bessada,‡ and R. W. Berg†

Department of Chemistry, Technical University of Denmark, Building 207,
DK-2800 Lyngby, Denmark, and CNRS-CRMHT, 1D, Avenue de la Recherche Scientifique,
45071 Orléans Cedex 2, France

Received April 30, 2002

The dissolution and complex formation of fluoroaluminates in two eutectic alkalifluoride mixtures, NaF–KF (FNAK) and LiF–NaF–KF (FLINAK), have been investigated by Raman, NMR, and thermal analysis. Melting and dissolution took place stepwise. The eutectic alkalifluoride mixtures with minor amounts of dissolved fluoroaluminate salts started melting at around 460 and 740 °C for FLINAK and FNAK mixtures, respectively. Total melting/dissolution of mixtures with 9–11 mol % aluminum fluoro salts added took place near 780 °C in the FLINAK solvent and at approximately 900 °C for FNAK solutions. The solidified melts were characterized by Raman bands at 561 (ν_1), 391 (ν_2), and 328 cm^{-1} (ν_5) and a ^{27}Al NMR chemical shift near 0 ppm originating from isolated AlF_6^{3-} octahedral ions. The Raman and NMR signals due to AlF_6^{3-} were also observed at temperatures where the samples were only partly melted. Upon total melting, a pronounced dissociation of AlF_6^{3-} into AlF_5^{2-} and fluoride ions took place. At even higher temperatures, the equilibrium was displaced in favor of AlF_5^{2-} in the FNAK solvent. The AlF_5^{2-} ion was characterized by an intensive Raman band at 558 cm^{-1} and an increasingly positive ^{27}Al chemical shift with raising temperature, e.g., of 16 ppm at 935 °C.

Introduction

AlF_6^{3-} ions are generally present as octahedral ions in many solid phases such as, e.g., cryolite and frozen solid mixtures made by dissolving AlF_3 in a sufficient excess of fluoride. The question about which species are present in the corresponding melts has been disputed since Gilbert and Materne[1] suggested the dominant existence of AlF_5^{2-} in 1990 (for articles related to this discussion see, e.g., ref 2).

In an attempt to investigate this question, we recently[2] studied the Raman spectra of AlF_3 or Na_3AlF_6 (cryolite) dissolved in FLINAK (i.e., the eutectic mixture of LiF−NaF−KF melting at around 450 °C). In this system, it was possible to study melts with fluoroaluminates in a much wider temperature region than what has been done with the alkali fluoride−aluminum fluoride binaries. From room temperature up to 750 °C it seemed clear that AlF_6^{3-} was the only fluoroaluminate species present for CR values (cryolite ratio, i.e., the alkalifluoride/AlF_3 molar ratio) between 8 and 23. The strong ν_1 stretching frequency of this complex proved to be very sensitive to the temperature; it changed continuously from 561 cm^{-1} at room temperature to 532 cm^{-1} at 750 °C. The Raman signal disappeared when we approached 800 °C because of fogging of the quartz container due to evaporation from the melt. No attempt to measure at higher temperature was done.

Subsequently, Auguste and Gilbert[3] have studied similar FLINAK mixtures at higher temperatures. At around 740 °C, their Raman spectra were temporarily very noisy and the intensities of the observed bands small. However, when the temperature was raised beyond 750 °C, their samples became transparent, and Raman spectra up to 915 °C could be quickly recorded in their setup, thus minimizing quartz degradation. Two bands in the 500−600 cm^{-1} region located at around 560 and 515 cm^{-1} could clearly be observed. These bands were, as assigned previously,[1] assigned to AlF_5^{2-} and AlF_6^{3-}, respectively.

In our work on Na_3AlF_6/AlF_3 dissolved in FLINAK, we noted that many melts had a cloudy appearance and solid

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* To whom correspondence should be adressed. E-mail: jvb@kemi.dtu.dk.
† Technical University of Denmark.
‡ CNRS-CRMHT.

[1] Gilbert, B.; Materne, M. *Appl. Spectrosc.* **1990**, *44*, 299−305.

[2] Brooker, M. H.; Berg, R. W.; von Barner, J. H.; Bjerrum, N. J. *Inorg. Chem.* **2000**, *39*, 3682−3689.

[3] Auguste, F.; Gilbert, B. In *Progress in Molten Salt Chemistry 1*; Berg, R. W., Hjuler, H. A., Eds.; Elsevier: Paris, France, 2000; pp 71−74.

10.1021/ic020305+ CCC: $25.00

particles were detected[2]. Auguste and Gilbert[3] also observed a similar behavior for their AlF_3−FLINAK mixtures up to 750 °C, claiming that their melts only were fully molten at temperatures above 750 °C.

In this work, we present new results on the fluoroaluminate complex formation in another eutectic fluoride solvent: NaF (40 mol %)−KF (60 mol %), in the following named FNAK, melting at around 721 °C according to refs 4 and 5. The methods of Raman and NMR spectroscopy were used to investigate the systems. The combination of these two kinds of measurements has previously proven to be a useful tool to understand binary NaF−AlF_3 melts.[6] The new results on FNAK−AlF_3 melts were supplemented by NMR spectra on FLINAK samples with similar CR values, which have previously only been studied by Raman spectroscopy[2]. Finally, thermal analysis up to 1000 °C was performed on different mixtures to investigate the melting behavior.

Experimental Section

The chemicals and purification procedures for the alkali fluorides (LiF, NaF, and KF) were the same as applied previously.[2] For most experiments, triple distilled AlF_3 (kindly supplied by Geir-Martin Haarberg, SINTEF Trondheim, Norway) was applied. Na_3AlF_6 (99.5% from Cerac Inc.) was used without further purification after being checked by Raman and IR spectroscopy. All handling and weighings were performed in argon filled gloveboxes (<5 ppm of H_2O). The eutectic alkali fluoride solvents were premixed under argon atmosphere (FLINAK at 700 °C and FNAK at 800 °C). The samples were prepared by the procedure previously applied.[2] Clear pieces of frozen solvent and appropriate amounts of the solute were melted together under dry argon atmosphere in a glassy carbon crucible (V25, Carbone Lorraine). The 11 mol % AlF_3 samples in FLINAK and FNAK were mixed at temperatures of 700 and 800 °C, respectively. The other FLINAK samples were typically mixed at around 600 °C.

Thermal Analysis. The measurements were performed in a stream of argon with two instruments: (i) A Setaram DSC multi HTC with a boron nitride crucible (AX05 from Carborundum, 4.5 mm inner diameter and 20 mm height) with a screw cap, designed and machined at CRMHT (CNRS-Orleans France), was used. Heating and cooling rates of 5 °C/min were applied. (ii) A Mettler type TA1 thermoanalyzer, in which a sample volume of 0.9 cm^3 was contained in a PtRh10 TG-DTA crucible (Mettler type T-DT-1), was used. After the crucible was filled with approximately 360 mg of sample and placed in the thermoanalyzer, the sample chamber was evacuated (0.1 Torr) and subsequently refilled/flushed with a stream (approximately 60 cm^3/min) of dry argon (Strandmøllen Industrigas, class 2,1.A ARD). A heating rate of 10 °C/min was applied.

Raman. Each sample (approximately 350 mg) was contained in a 4-holes windowless cell of graphite placed within argon filled (0.15 atm) quartz tube. The setup was heated in an alumina tube furnace (vertical height = 31 cm, inner diameter = 26 mm) equipped with insulation and a water-cooled outer brass housing. Four double quartz windows allowed the laser beam to pass and the scattered light to exit. Also, visual inspection of the melts was possible with this construction. The furnace was electrically heated by a Kanthal wire wound around the alumina tube. The temperature was controlled by means of a Pt/Pt10%Rh thermocouple and a PID regulator. The spectra were excited with an Ar^+-ion laser at a wavelength of 514.5 nm and recorded with a DILOR XY 800 mm focal length CCD spectrometer. Excitation took place with a vertically polarized beam and the scattered light was analyzed with a polarizer in horizontal (H) or vertical (V) orientation. Further details have been described previously.[2]

NMR. All NMR experiments have been carried out with a Bruker DSX 400 NMR spectrometer with a magnetic field of 9.4 T, operating at frequencies of 104.2 MHz for ^{27}Al and 376.3 MHz for ^{19}F. High temperature (HT) NMR experiments were acquired using the previously described[7] laser heated system developed at CRMHT (Orléans, France). Each sample was contained in a high purity boron nitride (BN AX05 from Carborundum) crucible, tightly closed by a screwed BN cap. The crucible was placed inside the RF coil, in the center of the cryomagnet, and heated by a continuous CO_2 laser beam ($\lambda = 10.6\ \mu m$). A ceramic shield thermally isolated the axial saddle coil. The high temperature NMR spectra were obtained using single pulse excitation consisting of 20 μs pulses, recycle delays of 500 ms, and 256 scans to obtain a reliable signal-to-noise ratio.

At room temperature, ^{27}Al and ^{19}F magic angle spinning (MAS) spectra have been acquired using high and very high-speed MAS probes from Bruker. The ^{27}Al high-resolution solid-state MAS NMR experiments were performed using 4 mm diameter rotors with a spinning rate of 12 kHz, very short pulses of 0.5 μs, recycle delays of 1 s, and 512 scans. ^{19}F MAS NMR spectra have been obtained with 2.5 mm diameter rotors allowing the instrument to reach spinning speeds of 35 kHz. Spectra were typically acquired with short pulses of 2 μs, recycle delays of 2 s, and 128 acquisitions.

^{27}Al and ^{19}F chemical shifts were referenced to 1 M aqueous solutions at room temperature of $Al(NO_3)_3$ and $CFCl_3$, respectively.

The NMR parameters (chemical shifts, line widths, quadrupolar coupling constants) were fitted to the experimental spectra by means of a modified version of the Winfit program[8] (from Bruker).

Results and Discussion

The sample concentrations are given as mole % of the solutes (AlF_3 or Na_3AlF_6) relative to the total number of moles (i.e., the sum of alkalifluorides and solutes). The cryolite ratio, CR, is defined as the molar ratio of alkali-fluorides (i.e. the sum of LiF, NaF and KF) to AlF_3. Na_3AlF_6 is formally considered to consist of 3 NaF and AlF_3 in the calculations of CR.

Thermal Analysis and Visual Observations. The DTA behavior when heating a sample with 11 mol % AlF_3 in FNAK from room temperature to 975 °C is shown in Figure 1A. Two peaks can be seen on the curve: The first one has its maximum at 738 °C and the second one at 879 °C. Gravimetric analysis revealed that virtually no evaporation took place in the measured temperature range. Visual inspection of the mixture, during the Raman experiments, showed that the sample was cloudy and only partly melted at 750 and 850 °C. At approximately 900 °C, clear melts

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(4) Sangster, J.; Pelton, A. D. *J. Phase Equilib.* **1991**, *12*, 511−537.

(5) Holm, J. L. *Acta Chem. Scand.* **1965**, *19*, 638−644.

(6) Robert, E.; Lacassagne, V.; Bessada, C.; Massiot, D.; Gilbert, B.; Coutures, J.-P. *Inorg. Chem.* **1999**, *38*, 214−217.

(7) Lacassagne, V.; Bessada, C.; Ollivier, B.; Massiot, D.; Florian, P.; Coutures, J.-P. *C. R. Acad. Sci. Paris, Ser. IIb: Solid State Chem. Cryst. Chem.* **1997**, *325*, 91−98.

(8) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70−76.

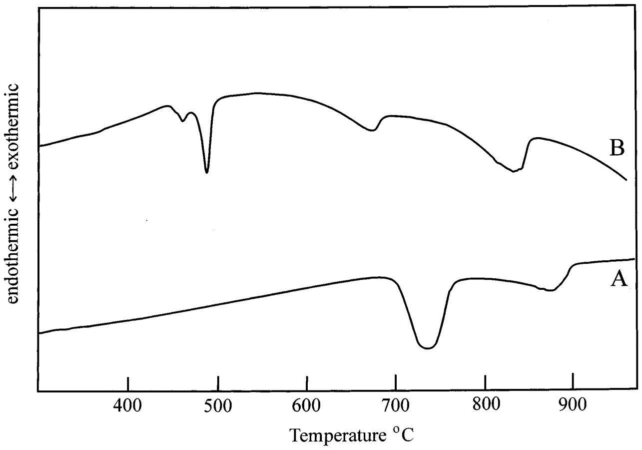

Figure 1. Thermal analyses upon heating. (A) DTA of 11 mol % AlF_3 dissolved in NaF−KF eutectic at a scan rate of 10 °C/min and (B) DSC of 11 mol % AlF_3 in LiF−NaF−KF eutectic, scan rate of 5 °C/min.

were obtained. According to the NaF−KF phase diagram,[4,5] the melting point for the eutectic NaF−KF should occur at 721 °C. It thus seems that the first signal on the DTA curve must be due to melting of the eutectic with some AlF_3 dissolved. The second signal (879 °C) can then be interpreted as due to total melting, i.e., an endothermic dissolution of the residual amount of AlF_3.

The DSC curve upon heating for a mixture with 11 mol % AlF_3 in FLINAK is shown in Figure 1B. The peaks in the region 450−490 °C are attributed to melting of the FLINAK solvent, and the endothermic feature at ∼830 °C is attributed to total dissolution/melting. The endothermic signal starting at approximately 600 °C probably is due to a phase transition in some of the solid particles (e.g., cryolite has a known transition[9] at ∼612 °C). Upon cooling of the sample from 980 °C, exothermic peaks were observed at similar temperatures. The first signal due to solidification appeared as a very sharp peak (at 810 °C).

Raman Measurements. Raman spectra of mixtures with 11 mol % AlF_3 dissolved in either FNAK or FLINAK (CR = 8) are shown in Figure 2. They were recorded on solid or partly melted samples from room temperature up to 750 °C.

The room temperature spectrum of 11 mol % AlF_3 in FNAK (Figure 2A) has two strong bands at 328 and 561 cm^{-1}, respectively, and a weak one at 391 cm^{-1}. No band was observed at higher wavenumbers. These band positions are similar to what was recently found for Na_3AlF_6 and AlF_3 in solidified FLINAK melts,[2] where bands were observed at 325, 380−390, and 561 cm^{-1} for CR values between 8 and 23. As previously done,[2] the 561 cm^{-1} band is ascribed to the ν_1 fundamental vibration, the 391 cm^{-1} band to the ν_2, and the 328 cm^{-1} band to the ν_5 mode from the octahedral AlF_6^{3-} ion in a matrix resembling that of elpasolite (K_2NaAlF_6). When the temperature was raised, the ν_1 band gradually shifted toward lower wavenumbers. At 750 °C, the ν_1 band occurred at 533 cm^{-1} (Figure 2B). The trend paralleled what was observed in the FLINAK solutions.[2] The ν_5 vibrational band for the FNAK mixture only showed a minor shift with temperature (from 328 cm^{-1} at room temperature to 322 cm^{-1} at 750 °C). It is interesting to note that for the two samples with CR = 8, i.e., for the AlF_3 (11 mol %)−FNAK mixture (Figure 2B) and the AlF_3 (11 mol %)−FLINAK mixture (Figure 2C), the band positions were practically identical at 750 °C.

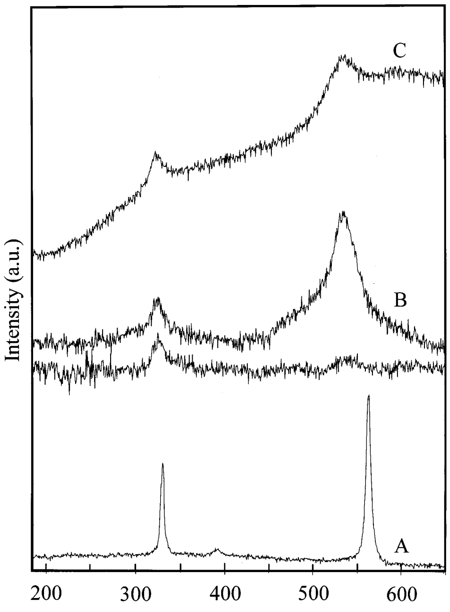

Figure 2. Raman spectra of 11 mol % AlF_3 solutions: (A) in NaF−KF at room temperature, (B) in NaF−KF at 750 °C (upper, polarized; lower, depolarized), and (C) in FLINAK at 750 °C.

As previously mentioned, the AlF_3−FNAK mixture did only partly melt at 750 °C. Nevertheless, it was possible to record the polarized and depolarized spectra shown in Figure 2B. It clearly appeared that the 533 cm^{-1} band must be polarized and the 322 cm^{-1} band depolarized in agreement with the assignment of the bands to ν_1 and ν_5, respectively, in octahedral AlF_6^{3-}. Such polarization behavior is typical of a liquid solution (or an isotropic medium), so we conclude that at least some aluminum fluoride must have been dissolved.

When the temperature was raised beyond 900 °C, a proper clear melt was obtained. Figure 3 shows Raman spectra for the AlF_3−FNAK mixture recorded at temperatures near the melting point. At 800 °C (Figure 3B, sample not totally molten), the band at around 533 cm^{-1} was broader than at 750 °C (Figure 3A). At 925 °C, i.e., just over the melting point, the spectrum had changed considerably (Figure 3C); a distinct Raman feature was still observed in the 500−600 cm^{-1} region, but the shape was different. Clearly, two bands now seem to be present: a major one with a maximum at ∼558 cm^{-1} and a shoulder at ∼530 cm^{-1}. A further increase of the temperature caused a gradual diminishing of the 530 cm^{-1} shoulder, which was only weakly seen at 975 °C (Figure 3D).

These changes in the Raman spectra of the 11 mol % AlF_3−FNAK mixture upon heating are much like the results found by Auguste and Gilbert[3] for their 3 mol % AlF_3 in FLINAK. Previously, it was discussed if Raman bands at

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(9) Yang, H.; Ghose, S.; Hatch, D. M. *Phys. Chem. Miner.* **1993**, *19*, 528−544.

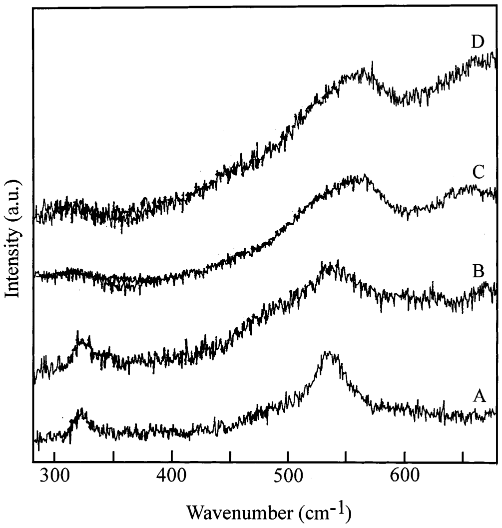

Figure 3. Raman spectra of 11 mol % AlF_3 in NaF−KF. (A) 750 °C, (B) 800 °C, (C) 925 °C, and (D) 975 °C.

around 500 cm^{-1} observed in fluoroaluminate melts without added oxide could be due to presence of oxide impurities. Gilbert and co-workers have analyzed many of their melts for oxide contamination by the Leco method, finding oxide contents too low to account for their 510 cm^{-1} Raman band.[10] Furthermore, from our recent results on the effect of adding oxide to fluoroaluminate−FLINAK melts,[11] it can be seen that the main band due to oxide species decreases in wavenumber with increasing temperature, changing from 509 cm^{-1} at room temperature to 493 cm^{-1} at 550 °C. Since the band positions for the aluminate species in general seem to be much the same in FNAK and FLINAK (see, e.g., Figure 2), we expect to find Raman signals below 490 cm^{-1} if oxide species would be present in the fully molten FNAK sample at 925 °C. Obviously, this is not the case. In the present study, the solutions have values of CR ranging from 8 to 23. For samples with such a large excess of fluoride ions, it seems unlikely that AlF_4^- should form. Further, it is well-known that this complex has its main Raman band near 622 cm^{-1} (see, e.g., refs 1, 6, and 10). No such band was observed in our Raman spectra. Consequently, the interpretation of the Raman spectra in the FNAK solvent must follow the lines proposed by Auguste and Gilbert:[3] During melting at around 900 °C, the AlF_6^{3-} ions dissociate extensively into fluoride and AlF_5^{2-} ions, as indicated by the appearance of the intensive 558 cm^{-1} Raman band. Thus, at melting and at higher temperatures the reaction

$$AlF_6^{3-} \rightleftarrows AlF_5^{2-} + F^- \tag{1}$$

must proceed to the right. As discussed extensively by Gilbert and co-workers, e.g., in refs 1, 3, and 6, the disappearance of AlF_6^{3-} explains the diminution of the 530 cm^{-1} band.

High Temperature ^{27}Al NMR. ^{27}Al NMR spectra were recorded on FLINAK samples containing dissolved Na_3AlF_6 or AlF_3. The cryolitic ratios (CR values) for these mixtures ranged between 8 and 23. When the temperature was raised from room temperature to above 600 °C, a small but significant ^{27}Al peak appeared for all our investigated samples. At 650 °C, chemical shifts near 4 ppm were found almost independently of the CR. A ^{27}Al chemical shift around 4 ppm has previously[7] been found for cryolite at 950 °C, i.e., just under the melting point. Cryolite in the high temperature phase contains discrete AlF_6^{3-} ions of almost perfect octahedral symmetry.[9] Thus, from the NMR similarity, it seems plausible that AlF_6^{3-} must be present in our FLINAK samples at temperatures around 650 °C. This view agrees well with the previously published[2] explanation of Raman spectra on the same samples.

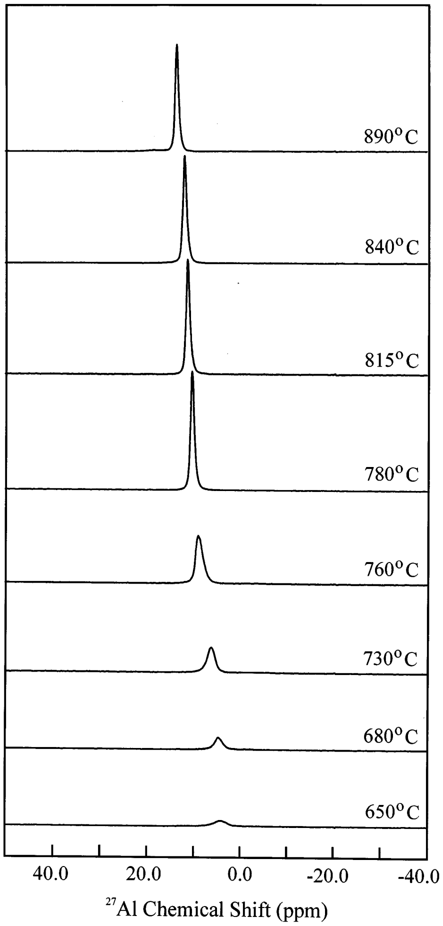

Figure 4. ^{27}Al NMR spectra of 11 mol % AlF_3 in FLINAK (CR = 8) as a function of temperature.

When the temperature was further raised, the ^{27}Al NMR signal became more intense and shifted toward higher ppm, see, e.g., Figure 4 for a mixture of 11 mol % AlF_3 in FLINAK, with CR = 8. Maximum intensities were reached at around 780 °C for this sample and for one with CR = 13 (9 mol % Na_3AlF_6 in FLINAK). For a FLINAK mixture with less Na_3AlF_6 added (5 mol %), the maximum intensity was reached at a slightly lower temperature, 730 °C. For some samples heated to high temperatures, decreasing signal strengths and line broadening were observed when the temperature approached 900 °C. For samples heated to even higher temperatures (∼1035 °C), a splitting of the signal into two bands was sometimes seen. This was probably due to

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(10) Robert, E.; Gilbert, B. *Appl. Spectrosc.* **2000**, *54*, 396−401.

(11) Brooker, M. H.; Berg, R. W.; von Barner, J. H.; Bjerrum, N. J. *Inorg. Chem.* **2000**, *39*, 4725−4730.

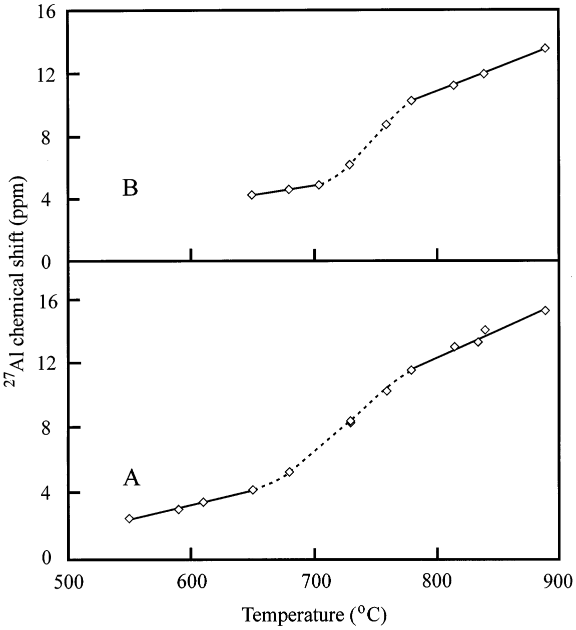

Figure 5. ^{27}Al NMR chemical shift as a function of temperature for (A) 9 mol % Na_3AlF_6 in FLINAK and (B) 11 mol % AlF_3 in FLINAK.

some evaporation of compounds from the melt. Post-experiment inspection of crucibles in which samples had been heated to such high temperatures showed that some salt had condensed on the inner side of the crucible lid. Previously performed[2] TGA experiments revealed that substantial weight loss from cryolite−FLINAK mixtures can occur at temperatures above 800 °C. It should be pointed out that the old measurements were performed in an open system under a flow of argon whereas the new NMR experiments were conducted with the melts contained in a closed vessel with minor evaporation.

The evolution of the NMR chemical shifts as a function of temperatures upon heating is shown in Figure 5 for two FLINAK samples with 9 mol % Na_3AlF_6 (Figure 5A) and 11 mol % AlF_3 (Figure 5B) added, respectively. In general, the ppm shift value of the aluminum NMR signal increased with temperature. At first, a linear increase with temperature was observed, and then, the ppm value increased steeply up to approximately 780 °C for both samples. In the region 780−890 °C, a continuous shift was again observed.

Even though some evaporation might have occurred at temperatures beyond 890 °C, we still have a clear ^{27}Al signal from the fluoroaluminate species in the melt on the NMR spectra at 935 °C. Chemical shifts of 15−16 ppm were typically observed for our FLINAK samples at this temperature.

In Figure 6, ^{27}Al NMR spectra of an 11 mol % solution of AlF_3 in FNAK (CR = 8) are shown at different temperatures. Upon heating, a single signal was observed at 890 °C (Figure 6A), becoming more intense and sharp when reaching 935 °C (Figure 6B). At 990 °C (Figure 6C), a decrease and some broadening of the peak was noticeable. As discussed for the FLINAK samples, this behavior might be explained by evaporation from the sample. Also, for the FNAK mixture an increase of the chemical shift with raising temperature can be observed (from 14 to 18.8 ppm at 890 and 990 °C, respectively). At 935 °C, a value of 17 ppm was found very similar to what was seen for the FLINAK mixtures at the same temperature.

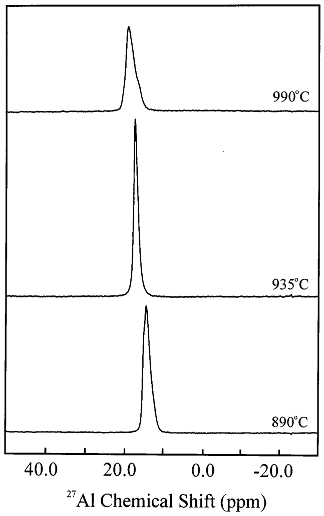

Figure 6. ^{27}Al NMR spectra of 11 mol % AlF_3 in NaF−KF eutectic (CR = 8) at various temperatures.

Discussion of the High Temperature NMR Results. The intensity of the NMR signal is proportional to the amount of aluminum in the liquid phase; i.e., it reflects directly the dissolution of fluoroaluminates into the melt. Thus, a maximum in intensity should indicate complete melting/dissolution. It also seems obvious to relate the nonlinear temperature dependence of the chemical shift to the process of melting. The observation that the intensity of the Al NMR signal is increasing considerably below and reaches its full size at about 780 °C (see Figure 4) is in accordance this view.

At 935 °C, the Al NMR spectra on a sample of 5 mol % AlF_3 in FLINAK with 5 mol % of Na_2O added have shown a band due to oxofluoroaluminate species at 43 ppm.[12] This is far more than what we observed for NMR spectra of AlF_3 dissolved in either FNAK or FLINAK at the same temperature (the band maximum was found at 15−17 ppm). It is not likely that the bands observed in the high temperature NMR spectra of the fully molten AlF_3−FNAK/FLINAK mixtures should arise from oxo species, and the different signal position confirms this interpretation. Previously, we obtained ^{27}Al NMR spectra[6] on NaF−AlF_3 melts having various compositions. For $X_{NaF} = 0.8$ (CR = 4) and 0.75 (CR = 3, pure cryolite), chemically shifted signals of 14.2 and 18.8 ppm were observed at ~1000 °C (i.e., over the melting point). For the same binary, at the eutectic NaF−cryolite composition ($X_{NaF} = 0.87$, CR = 6.7), Stebbins et al.[13] found a value of 13.3 ppm for the melt at 892 °C. As mentioned before, a shift of 4 ppm was found[6] for cryolite at 950 °C (just under the melting point). The change in the chemical shift upon melting was explained as due to the appearance of aluminumfluoro species with a coordination

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(12) Bessada, C.; Berg, R. W.; von Barner, J. H. Unpublished results.

(13) Stebbins, J. F.; Farnan, I.; Damdo, N.; Tzeng, S.-Y. *J. Am. Ceram. Soc.* **1992**, *75*, 3001−3006.

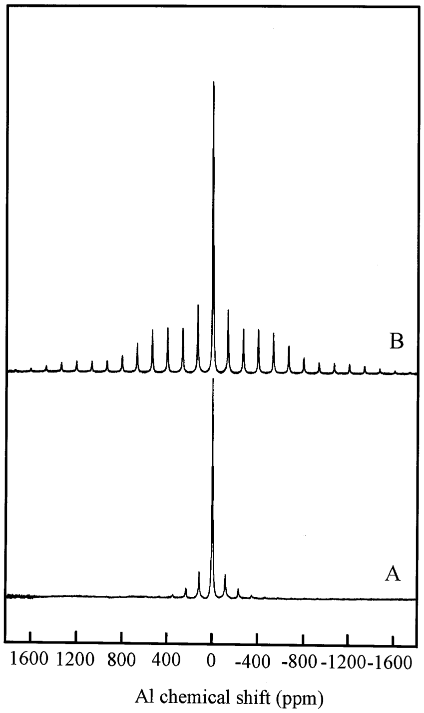

Figure 7. Room temperature ^{27}Al MAS NMR spectra of (A) solidified 9 mol % Na_3AlF_6 in FLINAK and (B) pure cryolite.

Table 1. ^{27}Al Chemical Shifts of AlF_6 Sites at Room Temperature in Various Surroundings

sample	^{27}Al chemical shift (ppm)	ref
Na_3AlF_6 (cryolite)	−1	7
Na_3AlF_6	0	13
K_2NaAlF_6 (elpasolite)	0.8	15
9% Na_3AlF_6 in FLINAK	−2.6	this work
5% AlF_3 in FLINAK	−0.4	this work
AlF_3	−15.9	this work

number less than six.[6,14] Apparently the NMR signals at 935 °C in FNAK and FLINAK solutions with CR = 8 indicate that the Al nuclei environments are very similar to what was seen in NaF−AlF_3 melts with CR ≥ 4.

^{27}Al and ^{19}F MAS (Magic Angle Spinning) NMR at Room Temperature. In Figure 7, the ^{27}Al MAS NMR spectra of pure Na_3AlF_6 and of Na_3AlF_6 (9 mol %) in FLINAK at room temperature are shown, both consisting of a sharp line centered near 0 ppm, with sets of sidebands due to spinning. A 5 mol % solidified solution of AlF_3 in FLINAK gave a similar ^{27}Al chemical shift (see Table 1). From the spectra, a quadrupolar coupling of 200 kHz can be calculated for the pure Na_3AlF_6 in agreement with what was found before.[7] For the fluoroaluminate solutions in FLINAK, a much lower value of 50 kHz was determined.

In general, hexafluoroaluminate compounds containing isolated regular AlF_6^{3-} octahedra have ^{27}Al chemical shifts in a narrow range (within a few ppm) around 0 ppm[7,13,15] (see Table 1). The signal is displaced toward more negative ppm values in case of fluorine bridging. AlF_3 may be seen as an example of a compound built up of AlF_6 octahedra sharing corners in a three-dimensional network.[16] For AlF_3, we found an ^{27}Al signal at −16 ppm. Thus, the observed ^{27}Al chemical shifts for fluoroaluminates in FLINAK occur in the region where signals due to isolated AlF_6^{3-} are expected. This fits well with the conclusions recently[2] drawn from Raman spectroscopic investigations on the same samples.

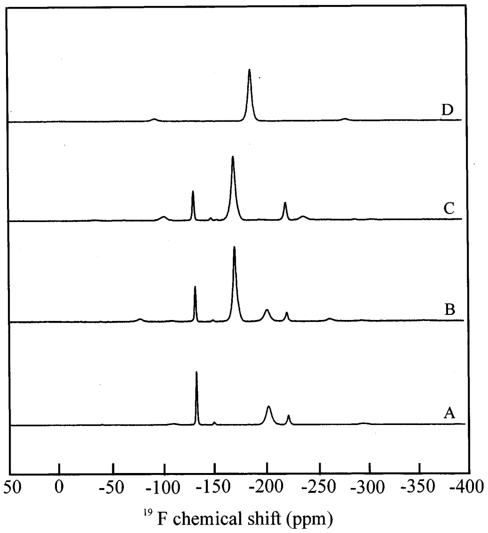

Figure 8. ^{19}F MAS spectra of (A) pure FLINAK, (B) 9 mol % Na_3AlF_6 in FLINAK, (C) 11 mol % AlF_3 in FNAK, and (D) pure cryolite.

Table 2. ^{19}F Chemical Shifts at Room Temperature for Various Compounds/Mixtures

sample	F(Alk)[a] sites (ppm)	FAl sites (ppm)
LiF	−204.4	
NaF	−224.8	
KF	−133.7	
FLINAK	−133.4, −205.0, −224.6	
5% Na_3AlF_6 in FLINAK	−133.6, −204.9, −224.2	−173.1
9% Na_3AlF_6 in FLINAK	−133.6, −204.8, −224.6	−173.0
11% AlF_3 in FNAK	−133.3, −224.8	−173.1
Na_3AlF_6 (cryolite)		−189.6

[a] Alk = Li, Na, K.

The ^{19}F MAS NMR spectra of pure alkali fluorides (LiF, NaF, and KF) all consisted of one sharp line (chemical shifts are given in Table 2). In the spectrum of the solidified FLINAK solvent (Figure 8A), ^{19}F lines at nearly the same position as for the individual salts were observed. Thus, the lines at −130, −210, and −225 ppm are assigned to KF, LiF, and NaF, respectively. These lines were also observed in spectra of the solidified FLINAK containing 9 mol % of dissolved Na_3AlF_6 (Figure 8B). In addition, a strong line appeared at −173 ppm. The sample of 11 mol % of AlF_3 in FNAK gave a similar intensive line at −173 ppm on top of the lines from NaF and KF (Figure 8C). The ^{19}F spectrum of pure cryolite (Figure 8D) consisted of a single line at around −190 ppm. A similar ^{19}F shift was previously ascribed to a FNa_3Al site in α-cryolite,[17] i.e., to F atoms interacting with both sodium and aluminum ions.

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(14) Bessada, C.; Lacassagne, V.; Massiot, D.; Florian, P.; Coutures, J.-P.; Robert, E.; Gilbert, B. *Z. Naturforsch.* **1999**, *54A*, 162−166.

(15) Dirken, P. J.; Jansen, J. B. H.; Schuiling, R. D. *Am. Mineral.* **1992**, *77*, 718−724.

(16) Hoppe, R.; Kissel, D. *J. Fluorine Chem.* **1984**, *24*, 327−340.

(17) Lacassagne, V.; Bessada, C.; Florian, P.; Bouvet, S.; Ollivier, B.; Coutures, J.-P.; Massiot, D. *J. Phys. Chem. B* **2002**, *106*, 1862−1868.

The chemical shifts at -173 ppm observed in the ^{19}F spectra of FLINAK and FNAK mixtures with added aluminum fluorides differ significantly from the value of -190 ppm observed for pure cryolite. We suggest that the -173 ppm signal arises from a F site only involving isolated AlF_6^{3-} octahedra. Some support for this interpretation may be found in recent work on ^{19}F NMR spectra of NaF$-$$AlF_3$ melts:[17] A value of -176 ppm was deduced for the ^{19}F signal from AlF_6^{3-} ions. In our diluted melts, the influence of the Na^+ ions would be expected to be of minor importance due to the longer average distance between Na^+ and the AlF_6^{3-} octahedra compared to what is the case for cryolite in the solid state.

Conclusions

From the thermal experiments on 11 mol % AlF_3 solutions in FLINAK and FNAK, it seems clear that the melting of the mixtures took place over a range of temperatures. At first, the solvents melted (FLINAK at around 460 °C and FNAK near 740 °C) with some limited dissolution of the aluminum fluoro salts. Complete melting and dissolution took place at much higher temperatures: for the FLINAK solution near 800 °C, and for the FNAK solution at around 880 °C. The HT NMR measurements showed that the ^{27}Al signal reached a maximum in intensity at a temperature of 780 °C and ~935 °C for FLINAK and FNAK mixtures, respectively. Further, the observations done in connection with the Raman experiments revealed that the melts became transparent at these temperatures, indicating total melting. Also, recent ICP measurements[18] seem to be in accordance with this: The solubility of cryolite in FLINAK was determined to be about 7 mol % at 730 °C and by extrapolation seems to reach over 10 mol % at 780 °C. Thus, there is little doubt that melting and dissolution took place in several steps.

This behavior explains why AlF_6^{3-} according to Raman measurements[2,3] is the dominating species in FLINAK melts at lower temperatures. To start, only a small amount of the aluminum fluorides will dissolve, and the melt will have an actual CR value much higher than the one calculated from the weights; i.e., the amount of fluoride relative to aluminum is very high. If we consider the results of Østvold and coworkers[18] for the solubility of cryolite in FLINAK, e.g., a CR of more than 550 can be calculated for the molten phase at 550 °C. Thus, equilibrium 1 will be drastically shifted in favor of AlF_6^{3-} due to the high proportion of fluoride to AlF_3.

From the NMR measurements at high temperatures, it seems safe to conclude that a ^{27}Al chemical shift near 4 ppm is typical for the octahedral AlF_6^{3-} ion at 650 ° C. An increase of the chemical shift can be correlated with a decrease in the average fluoride coordination number of aluminum.

The ^{27}Al MAS NMR spectra of solidified melts of cryolite or AlF_3 in FLINAK indicated that regular AlF_6^{3-} octahedra were present. Also, ^{17}F MAS NMR spectra were interpreted as to be in favor of the presence of isolated AlF_6^{3-} ions in the solid state.

The Raman and NMR results on fully molten $AlF_3$$-$FNAK mixtures with CR = 8 indicate that in this melt the dominating aluminumfluoro complex is AlF_5^{2-}.

Finally, the high temperature NMR results on solutions of AlF_3/Na_3AlF_6 in FLINAK with high CR values (between 8 and 23) fit well with AlF_6^{3-} and AlF_5^{2-} being the major species in partly and fully molten mixtures, respectively. Thus, the presence of AlF_5^{2-} proposed by Auguste and Gilbert[3] to explain the Raman spectra of such melts is supported.

In conclusion, the evidence for the existence of AlF_5^{2-} is quite strong.

Acknowledgment. The authors are grateful for financial support from EEC ARI Contract HPRI-CT-1999-00042. Further thanks are due to the French Foreign Ministry (The French Embassy in Copenhagen) for travel support.

IC020305+

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(18) Tkatcheva, O.; Mediaas, H.; Østvold, T. Personal communication.